

# Aryl Cations from Aromatic Halides. Photogeneration and Reactivity of 4-Hydroxy(methoxy)phenyl Cation

Stefano Protti, Maurizio Fagnoni,\* Mariella Mella, and Angelo Albini\*

Dipartimento di Chimica Organica, Università, V. Taramelli 10, 27100 Pavia, Italy

fagnoni@unipv.it

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The photochemistry of 4-chlorophenol (1) and 4-chloroanisole (2) has been examined in a range of solvents and found to lead mainly to reductive dehalogenation, through a homolytic path in cyclohexane and a heterolytic path in alcohols. Heterolysis of 1 and 2 in methanol and 2,2,2-trifluoroethanol offers a convenient access to triplet 4-hydroxy- and 4-methoxyphenyl cations. These add to  $\pi$  nucleophiles, viz., 2,3-dimethyl-2-butene, cyclohexene, and benzene, giving the arylated products in medium to good yields. Wagner–Meerwein hydride and alkyl migration are evidence for the cationic mechanism of the addition to alkenes. Arylation (with no rearrangement) was obtained to some extent also in nonprotic polar solvents such as MeCN and ethyl acetate, reasonably via an exciplex and with efficiency proportional to the nucleophilicity of the trap (2,3-dimethyl-2-butene > cyclohexene  $\gg$  benzene).

### Introduction

The direct formation of an aryl-alkyl or an aryl-aryl bond has received much attention in the past years in view of its application to the synthesis of natural products and organic conducting materials.<sup>1</sup> This goal has been achieved generally starting from aromatic halides by means of organometal-mediated reactions. Among these, palladium-catalyzed coupling is the most studied reaction and has been applied in industrial processes for fine chemical synthesis.<sup>1d</sup> Recently we have developed an alternative photochemical path for the formation of an aryl-carbon bond using aromatic monohalides (chlorides or fluorides) as precursors. The method is based upon the generation of aryl cations that readily form new C-Cbonds. The reaction occurs efficiently with 4-chloro- and 4-fluoroanilines and the corresponding N,N-dimethyl derivatives.<sup>2</sup> The aryl cation adds to  $\pi$  nucleophiles such as alkenes,<sup>2a</sup> aromatics,<sup>2a</sup> and heteroaromatics.<sup>2c</sup> It appears that a photochemical  $S_N1$  path via aryl cation is viable for aryl-carbon bond formation, provided that some conditions are met: (a) The aromatic ring bears a strong electron-donating substituent in order to make photoheterolysis of the carbon-halogen bond permissible. (b) ISC is efficient and the fragmentation occurs from the triplet in order to generate the phenyl cation likewise as a triplet.<sup>3</sup> (c) A polar solvent such as MeCN, MeOH, or 2,2,2-trifluoroethanol (TFE) is used.

To widen the scope of the reaction, we considered chlorophenols and chloroanisoles as further potential phenyl cation precursors meeting the above requirements. Differently from chloroanilines, the photochemistry of these substrates has been previously investigated in detail. Chlorophenols are largely used both in agriculture and in industry as antimicrobials, and their release in the environment has required investigations on their photostability, also with regard to the possible photoformation of the highly toxic polychlorodioxins from polyhalophenols.<sup>5</sup> As a consequence, most of these studies were carried out in water rather than in organic media. In the case of 4-chlorophenol efficient dehalogenation was reported to occur via two paths. Earlier studies in aqueous alkali<sup>6</sup> and in MeOH<sup>7</sup> were interpreted as a homolytic fission. More recently, the photoreactivity of *p*-chlorophenol in water was explained by invoking a carbene, 4-oxocyclohexa-2,5-dienylidene, as the key intermediate for the above reactions (see Scheme 1, path a).<sup>8</sup> This species could arise through deprotonation of 4-hydroxyphenyl cation, but no reaction was attributed to the latter intermediate (path *b*).

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<sup>(3)</sup> Differently from the triplet, singlet aryl cations behave as unselective electrophiles and reaction with the solvent is usually observed also in the presence of  $\pi$  nucleophiles. See ref 4

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## SCHEME 1



In the case of 4-chloroanisole, irradiation led to two processes, photoreduction to yield anisole and photosubstitution of the chlorine atom to give aryl ethers in alcohols. Several mechanistic hypotheses have been presented. For example, Pinhey supposed that the first process involved photohomolysis and the latter resulted from the attack by the solvent onto an excited state of anisole.9 Photosubstitution was also explained by the attack of the solvent onto the radical cation of chloroanisole resulting from photostimulated emission of an electron.<sup>10</sup> On the contrary, the radical anion of 4-chloroanisole was invoked by Siegman et al. as the intermediate in the formation of aryl ethers. The radical anion resulted from photoinduced electron transfer from the solvent (MeOH).<sup>11</sup> In aqueous media or MeCN/water solutions the formation of an excimer was proposed, and both the radical cation and the radical anion of the haloanisole could be formed.<sup>12</sup> In addition, the presence of strong electron-donating alkenes such as 1,1-diphenylethylene in the reaction medium caused assisted homolytic photodehalogenation.<sup>13</sup>

Thus, the matter has not been fully clarified, and we deemed it worthwhile to reconsider the photochemistry of 4-chlorophenol (1) and 4-chloroanisole (2) in different solvents and in the presence of  $\pi$  nucleophiles to assess whether the appealing triplet aryl cation chemistry could be obtained also from these compounds, even if there was no indication of it in the literature.

### Results

Irradiation in Neat Solvent The photoreactivity of 1 and 2 was first examined in 0.05 M solutions in five solvents, viz., cyclohexane, ethyl acetate, MeCN, methanol, and TFE by irradiation at 310 nm (see Table 1 and Scheme 2). Two sets of experiments were carried out, the first by irradiating for a fixed time (14 h) and the latter by irradiating up to total consumption of the starting halide for preparative experiments. In some cases it was found that the material balance was unsatisfactory. Apparently, this was due to thermal reactions of the phenols induced by hydrochloric acid liberated in the photoreaction, since the balance was better when the experiments were carried out in the presence of an equimolar amount of cesium carbonate as a buffering agent.<sup>14</sup> The process occurring was reductive photodechlorination yielding phenol 3, though with different

 TABLE 1. Irradiation of 4-Chlorophenol (1) in Neat

 Solvent

	<b>1</b> (0.05 M)		$1 + Cs_2CO_3$ (0.025 M)	
solvent	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )
cyclohexane	38	<b>3</b> , 23	30	<b>3</b> , 30
ethyl acetate	11	<b>3</b> , 9	51	<b>3</b> , 30
acetonitrile	23	<b>3</b> , <1	24	<b>3</b> , 23
methanol	100	3, 96	100	3, 94
ГFE	52	3, 8	80	3, 56 (66)
		<b>4</b> , tr		4, 5 (6)

<sup>*a*</sup> The consumption and the products yield after 14 h of irradiation were determined by GC. In parentheses are the isolated yields after total consumption of the starting halide.

# **SCHEME 2**



	<b>2</b> (0.05 M)		$2 + Cs_2CO_3 (0.025 \text{ M})$	
solvent	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )
cyclohexane	88	5, 80	93	5, 87
ethyl acetate	11	5, 4	9	<b>5</b> , 5
acetonitrile	5	<b>5</b> , 3	17	5, 2
methanol	47	5, 30	60	5, 42
		<b>6</b> , tr		<b>6</b> , tr
		7, 14		7, 17
TFE	48	5, 9	66	5, 21 (32)
		6, 23		6, 13 (18)
		<b>8</b> , 10		8, 10 (12)
<sup>a</sup> Condition	s, see Table 1.			

efficiency (maximal in MeOH). A low yield of a further photoproduct was isolated in TFE, viz., 2,4'-hydroxy-5-chlorobiphenyl **4**, whereas bicyclohexyl was found in cyclohexane.

Irradiation of **2** caused likewise an efficient photoreduction leading to anisole (**5**). The fastest conversion was in this case obtained in cyclohexane (where some bicyclohexyl was formed), whereas the reaction in polar aprotic solvents was slow (Table 2 and Scheme 2). 2,4'-Dimethoxy-5-chlorobiphenyl (**6**, the analogue of **4** from **1**) was formed in a modest yield in TFE (20%) and only in traces in MeOH. Differently from the case of **1**, small

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<sup>(14)</sup> The salt is completely soluble in MeOH or TFE but slightly soluble in the other solvents.

TABLE 3.Irradiation of 1 and 2 in the Presence of 0.5M 2,3-Dimethyl-2-butene

	<b>1</b> (0.05 M)		<b>2</b> (0.05 M)	
solvent	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )
cyclohexane	$54^b$	<b>3</b> , 13 <b>9</b> , 10	84	<b>5</b> , 1 (2) <b>12</b> , 28 (34) <b>13</b> , 3 (4)
ethyl acetate	77	<b>3</b> , 15 (20) <b>9</b> , 53 (69)	50	<b>5</b> , 4 (7) <b>12</b> , 27 (54)
acetonitrile	44	<b>3</b> , 8 (9) <b>9</b> , 27 (67)	31	<b>5</b> , <1 (2) <b>12</b> , 15 (49)
methanol	100	<b>3,</b> (61) <b>9</b> , (22)	100	5, 18 12, 21 13, 18 14, 10
$\begin{array}{c} methanol + \\ Cs_2CO_3 \end{array}$	100	<b>3,</b> (45) <b>10</b> , (26)	88	<b>5</b> , 20 (22) <b>12</b> , 14 (16) <b>13</b> , 15 (17) <b>14</b> 14 (17)
TFE	91	3, 22 9, 15 11, 18	78	<b>5</b> , 16 <b>12</b> , 10 <b>13</b> , tr <b>15</b> , 7 <b>16</b> 11
$\begin{array}{c} TFE + \\ Cs_2CO_3 \end{array}$	100	3, (19) 9, (43) 11, (12)	100	<b>5</b> , (12) <b>12</b> , (21) <b>13</b> , (14) <b>15</b> , (17) <b>16</b> (8)

 $^a$  Conditions, see Table 1.  $^b$  No further consumption after prolonged irradiation.

### **SCHEME 3**



amounts of aryl ethers 1,4-dimethoxybenzene (7, 17%) and 4-(2,2,2-trifluoroethoxy)anisole ( $\mathbf{8}$ , 10%) were obtained from  $\mathbf{2}$  in the two alcohols tested.

**Irradiation in the Presence of**  $\pi$  **Nucleophiles.** We next explored the reactions of **1** and **2** when irradiated in the above solvents in the presence of  $\pi$  nucleophiles. 2,3-Dimethyl-2-butene, cyclohexene, and benzene were chosen for this purpose.

Since the acidity liberated may affect the results (e.g., by inducing polymerization of the alkene), a second set of experiments in the presence of equimolar  $Cs_2CO_3$  was carried out. The results of these experiments are reported only when differing from what observed in the absence of the salt. Also in this case, the results from the irradiation for a fixed time (14 h) and at total consumption are reported.

**Irradiation of 1 and 2 in the Presence of 2,3-Dimethyl-2-butene.** In the presence of 0.5 M 2,3dimethyl-2-butene, 4-chlorophenol was converted to a somewhat larger degree than in neat solvents (see Table 3 and Schemes 3 and 4). The products were phenol (3) and an alkylated product, 2,3-dimethyl-3-(4-hydroxySCHEME 4



phenyl)-1-butene (9), obtained in a satisfactory yield (ca. 70%) in ethyl acetate or acetonitrile. In alcohols, the results were somewhat different, both because of the greater importance of reduction to **3** in MeOH and because compound **9** was accompanied or substituted by the corresponding  $\beta$ -alkoxyalkyl derivatives **10** (in MeOH, only in the presence of Cs<sub>2</sub>CO<sub>3</sub>) and **11** (in TFE).

With 4-chloroanisole, reduction to **5** was generally less important (<20%); addition of the alkene was quite efficient but was varied with regard to the structure of the final product (Table 3 and Scheme 4). Thus, arylbutene **12** was the exclusive or largely dominant product in aprotic solvents, whereas it was accompanied by arylbutane **13** and by the 3-alkoxy-2-arylbutanes **14** and **15** in alcohols. (Actually in TFE there was also a further adduct, 2-alkoxy-2-arylbutane **16**.) The presence of the base increased somewhat the yield of the photoproducts.

Irradiation of 1 and 2 in the Presence of Cyclohexene. The results of the irradiations in the presence of 0.5 M cyclohexene are reported in Table 4 and Schemes 5 and 6. Reduction was again more important with chlorophenol 1 (62% in MeOH, 20-30% with other solvents) than with chloroanisole 2 (15–25%). Photolysis of 1 in nonprotic solvents gave trans 1-(4-hydroxyphenyl)-2-chlorocyclohexane (17) as the only adduct in moderate yield. In MeOH a small fraction of adducts was obtained, and because their separation was difficult, the raw photolisate was treated with methyl iodide. Separation then afforded three photoproducts, viz., 1-(4-methoxyphenyl)-1-methoxycyclohexane (18), 1-(1-(4-methoxyphenyl)-1-methoxy)methylcyclopentane (19), and trans 1-(4methoxyphenyl)-2-chlorocyclohexane (20) in a ca. 10% overall yield. The reaction in TFE yielded again three adducts, viz., the chlorocyclohexane 17 and the two ethers 1-(1-(4-hydroxyphenyl)-1-(2,2,2-trifluoroethoxy)methylcyclopentane (21) and 1-(p-hydroxyphenyl)-1-(2,2,2-trifluoroethoxy)cyclohexane (22). In TFE the yield of adducts to cyclohexene considerably increased in the presence of cesium carbonate.

As for chloroanisole **2**, arylchlorocyclohexane **20** was formed in aprotic solvents. In alcohols the results were more varied, and two ethers (**18** and **19**) were obtained

# **TABLE 4.** Irradiation of 1 and 2 in the Presence of 0.5M Cyclohexene

	<b>1</b> (0.05 M)		<b>2</b> (0.05 M)	
solvent	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )
cyclohexane	$48^{b}$	<b>3</b> , 21 <b>17</b> , tr	66	<b>5</b> , 11 (16) <b>20</b> , 25 (38)
ethyl acetate	56	<b>3</b> , 18 (24) <b>17</b> , 5 (20)	50	<b>5</b> , 8 (15) <b>20</b> , 18 (32)
acetonitrile	25	<b>3</b> , 7 (18) <b>17</b> , tr (12)	12	<b>5</b> , 5 (26) <b>20</b> , 7 (20)
methanol	100 <sup>c</sup>	<b>5</b> , (62) <b>18</b> , (tr) <b>19</b> , (8) <b>20</b> , (4)	83	<b>5</b> , 17 (18) <b>18</b> , 31 (32) <b>19</b> , 11 (15)
TFE	79	<b>3</b> , 27 (30) <b>17</b> , 6 (8) <b>21</b> , 5 (6) <b>22</b> , (4)	80	<b>5</b> , 9 (11) <b>20</b> , 24 (29) <b>23</b> , 37 (45)
$\begin{array}{c} TFE + \\ Cs_2CO_3 \end{array}$	100	<b>3</b> , (44) <b>17</b> , (12) <b>21</b> , (13) <b>22</b> , (tr)	100	<b>5</b> , (10) <b>20</b> , (9) <b>24</b> , (20) <b>25</b> , (21)

 $^a$  Conditions, see Table 1.  $^b$  No further conversion obtained by prolonged irradiation.  $^c$  The raw photolisate was methylated with CH<sub>3</sub>I before separation by column chromatography (see Experimental Section).

### **SCHEME 5**



in methanol, and in neat TFE chloro derivative **20** was formed along with arylcyclohexane **23**. On the other hand, although the presence of  $Cs_2CO_3$  did not change the result in MeOH, in TFE this led to the formation of two trifluoroethyl ethers, the 1-(4-methoxyphenyl)cyclohexyl derivative **24** and the 1-(4-methoxyphenyl)-1-cyclopentylmethyl derivative **25**, along with compound **20**.

As in the reaction with 2,3-dimethyl-2-butene compounds **7** and **8** were not detected in any of the irradiations in the presence of alkenes.

**Irradiation of 1 and 2 in the Presence of Benzene.** The results of the irradiations in the presence of 1 M benzene are shown in Table 5 and Scheme 7. With both compounds **1** and **2**, reduction to **3** (or **5**) predominated, particularly with the first one (88% yield of phenol in MeOH). However, 4-phenylphenol (**26**) and 4-phenylanisole (**27**) were isolated in ca. 70% yield in TFE. Further

#### **SCHEME 6**



TABLE 5.Irradiation of 1 and 2 in the Presence of 1 MBenzene

	<b>1</b> (0.05 M)		<b>2</b> (0.05 M)	
solvent	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )	consumption <sup>a</sup> (%)	products (% yield <sup>a</sup> )
cyclohexane	36	<b>3</b> , 21	85	<b>5</b> , 75 <b>27</b> , tr
ethyl acetate	23	<b>3</b> , 9 <b>26</b> , tr	25	5, 6 27, 8
acetonitrile	10	3, 7 26. tr	12	5, 4 27, 4
methanol	100	<b>3</b> , 88 <b>26</b> , 10	40	<b>5</b> , 12 <b>27</b> , 5
TFE	63	<b>3</b> , 11 (16) <b>26</b> , 50 (66)	54	<b>5</b> , <1 (6) <b>27</b> , 20 (70)

<sup>a</sup> Conditions, see Table 1.

**SCHEME 7** 



points worth noting are the increased efficiency in the reduction of 2 in the presence of benzene in cyclohexane and the fact that a large amount of additive was required for affecting the photoreactions when using benzene (1 M) than when using the previous alkenes (0.5 M).

### Discussion

The above results show that, as hoped, the photoreactivity of 4-chlorophenol (1) and 4-chloroanisole (2) can be exploited for the arylation of  $\pi$  nucleophiles such as alkenes and aromatics, similarly to what was previously observed with haloanilines.<sup>2</sup> The pattern of reactivity observed is quite varied, however, and depends on the solvent chosen.

**Photoreaction of 4-Chlorophenol.** Intersystemcrossing (ISC) is known to be close to unitary with chlorophenol **1** both in nonpolar (*n*-hexane) and polar solvents (water),<sup>8a</sup> and thus the reaction is attributed to the triplet state. Laser flash photolysis studies allowed detection of  $\mathbf{1}^{3^*}$  only in nonpolar solvents, and in polar or protic solvents this transient became too short-lived to be detected. Thus, the photoreaction in cyclohexane can be attributed to homolytic fragmentation and hydrogen abstraction from the solvent by the aryl radical, as supported by the formation of bicyclohexyl.

In ethyl acetate and acetonitrile, 4-chlorophenol is markedly less photoreactive, reasonably because of the shorter lifetime of the triplet in this case.<sup>15a</sup> The low reactivity in acetonitrile ( $\Phi \approx 0.002^{8a}$ ) contrasts with the rather efficient fragmentation of 4-chloroaniline in this solvent ( $\Phi = 0.44^{8b}$ ). Phenol **1**, however, does give arylation reactions in these solvents and indeed also in cyclohexane. The efficiency of such process depends on the nucleophilicity (or electron donor ability) of the trap used, 2,3-dimethyl-2-butene > cyclohexene  $\gg$  benzene. We suggest that this involves the formation of an exciplex between **1**<sup>3\*</sup> and the nucleophile as the reaction intermediate (compare below the case of 4-chloroanisole).

In protic solvents, the triplet undergoes heterolytic fragmentation<sup>8a</sup> and a triplet aryl cation is formed. This gives phenol 3 as the main product. The process is thought to involve hydrogen abstraction from the solvent to yield a radical cation intermediate and subsequent reduction by the solvent (or the nucleophile used) to closed-shell, neutral 3. Alternatively, the aryl cation is trapped by the starting phenol to yield a small amount of dihydroxybiphenyl **4**. Addition of a  $\pi$  nucleophile traps the intermediate. Since any cations are very short-lived species,<sup>2</sup> a relatively high amount of the nucleophile (0.5 M alkenes, 1 M benzene) is required in order to make this reaction efficient. Even with this large excess, in MeOH 4-hydroxyphenyl cation is effectively reduced through a different mechanism. This path involves deprotonation (Scheme 1) and hydrogen abstraction by the carbene, as demonstrated by Grabner,<sup>8a</sup> and remains predominant (>60%) in this solvent, limiting the arylcarbon bond formation from 1. TFE stabilizes the cation and is the solvent of choice for arylation reactions. In this solvent, arylation consistently predominates with both 1 and 2 and, contrary to the case of aprotic solvents, does not depend on the nucleophilicity of the trap used. Arylation of benzene to yield 26 (Scheme 8) requires no further comment. As for the addition onto alkenes, this is envisaged as involving a phenonium ion as an intermediate<sup>16</sup> as illustrated in the reaction with 2,3-dimethyl-2-butene in Scheme 8, analogously to the case of 4-aminophenyl cation.<sup>17</sup>

In non-nucleophilic solvents, deprotonation of the adduct cation affords allylphenol **9** in a satisfactory yield (path *a*). In alcohols, the phenonium ion intermediate undergoes competitive nucleophilic attack by the solvent, giving the corresponding ethers **10** and **11** (path *b*). Cesium carbonate has an effect here. In MeOH, addition of this salt favors methoxide addition to form  $\beta$ -alkoxy-derivative **10**, whereas in TFE it is the base-induced

**SCHEME 8** 



R = H, Me;  $R' = CH_3$ ,  $CF_3CH_2$ 

SCHEME 9



deprotonation that increases (9 grows from 16% to 43%), the yield of trifluoroethoxy ether **11** not changing appreciably.

Essentially the same reactions are observed in the presence of cyclohexene (Scheme 9). Arylation of the alkene is here less efficient, and the evolution of the intermediate phenonium ion in part different. Deprotonation is not observed, apparently because of the unfavorable alignment of the C–H cyclopropane bond with the positively charged  $\pi$ -system, and the expected 1,2-addition derivatives are formed only when chloride is the nucleophile and then in a regioselective (*trans*) fashion (Scheme 9, path *a*). This led to chlorinated **17**, formed in a higher amount in nonalcoholic solvents and absent in MeOH, where reduction overcomes any other photoprocess.

Noteworthy, the most abundant products in TFE and a significant proportion in MeOH contain a rearranged alkyl chain. The processes occurring are classical carbocation rearrangement at the phenonium ion level.

<sup>(15) (</sup>a) Laser flash photolysis experiments on 4-chlorophenol in acetonitrile did not reveal any triplet signal. See ref 8a. (b) Evidence for a similar mechanism in the reduction of the analoguous 4-aminophenyl cation has been presented; see ref 2b. A study on the mechanism of the photoreaction of 1 in alcoholic solvents is underway.

<sup>(16)</sup> We have no positive evidence for the phenonium structure of the adduct cation, but this is calculated to be the lowest-lying adduct with an alkene; see ref 2a.

<sup>(17)</sup> Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2003**, *68*, 1067–1074.

Wagner–Meerwein hydride shift (path *b*) and solvent addition lead to benzyl ethers **18** and **22**, while alkyl rearrangement causes ring contraction to yield cyclopentylmethyl ethers (path *c*). The occurrance of these rearrangements further supports the cationic course of the reaction and is reminescent of the formation of cyclopentylmethyl derivatives in the photoreaction of 4-haloanilines in the presence of cyclohexene and amines.<sup>17</sup>

Photoreaction of 4-Chloroanisole. Most of the above considerations on 4-chlorophenol can be extended to 4-chloroanisole. The fact that the photoreaction is most efficient in cyclohexane fits with previous report,18 and the formation of anisole 5 and bicyclohexyl support that homolysis from the triplet is involved. The triplet has been identified as a relatively long-lived species ( $\tau$  900 ns) in perfluorohexane.<sup>12</sup> The reaction is quite inefficient in polar, aprotic solvents. Indeed, in acetonitrile a broad band at 420-500 nm has been observed by laser flash photolysis and attributed to the ion pair  $(2^{+}/2^{-})$  from the triplet state.<sup>12</sup> This complex was reported to decay unproductively to the ground state.<sup>12</sup> In alcohols, photoheterolysis is the main process, giving 4-methoxyphenyl cation. Obviously, whereas 4-hydroxyphenyl cation easily deprotonates in these solvents, 4-methoxyphenyl cation can undergo no such cleavage and the triplet carbene pathway is precluded. Therefore, although reduction to anisole remains efficient in MeOH, trapping has more chance. Dimethoxybiphenyl 6 is formed in trace amount in MeOH but in >20% yield in TFE. Furthermore, aryl ethers **7** and **8** are obtained in both alcohols (10-17%). Because these compounds are not formed in irradiations with alkenes or benzene, it is reasonable that they arise from the same intermediate. Triplet aryl cations are not expect to add to  $\sigma$  nucleophiles. These species are not localized cations and rather have a diradical nature, with a carbene character at the divalent carbon. This is supported by previous calculations and experimental studies on the analoguous 4-aminophenyl cation, where likewise no solvent addition takes place,<sup>2a,4</sup> and well explains both reduction by hydrogen-donating solvents and addition to nucleophiles observed also in the present case. Unlike the triplet, singlet aryl cations add efficiently even to relatively poor  $\sigma$  nucleophiles, e.g., to acetonitrile.<sup>3,4</sup> Thus, formation of the ethers may involve ISC from the initially formed triplet to the low-lying singlet cation in solution (for an analoguous proposal, see ref 4).<sup>19</sup> Paths not involving photoheterolysis, such as electron transfer from the solvent<sup>11</sup> or photostimulated ionization of the aromatic compound (important in water),<sup>10,12</sup> have been suggested in related cases but appear unlikely in the present reaction in alcohols. Likewise, alkene-assisted photodehalogenation has been invoked by Arnold for the reaction of some aryl halides with arylolefins<sup>13</sup> but does not apply to weak donors such as the present aliphatic traps.

The reaction with 2,3-dimethyl-2-butene follows qualitatively the same pattern as with **1**. Deprotonation of the phenonium ion (path *a*) to yield allylanisole derivative **12** is more important under all conditions (33% in cyclohexane). A specific path is formation of some (<20%) aryl*butane* **13** under some conditions. This may result from the stabilization through intramolecular electron transfer in the phenonium ion (path *d*, Scheme 8), leading to a diradical structure in the intermediate and facilitating hydrogen abstraction. A similar mechanism has been invoked for the reaction of the 4-*N*,*N*-dimethylaminophenyl cation with norbornadiene.<sup>20</sup> In alcohols, methyl and trifluoroethyl ethers were formed, including Wagner–Meerwein rearranged product **16** (path *c*, Scheme 8), more abundant in TFE than unrearranged **15**.

With cyclohexene, *trans* 1-aryl-2-chlorocyclohexane **20** is the main product in nonprotic solvent, whether polar or apolar solvents. In MeOH, rearranged ethers (both H and alkyl shift, paths *b*, *c*, Scheme 9) were formed in a better yield than from phenol **1**, as a result of the lower proportion of photoreduction (18% rather than 62%). Interestingly, in neat TFE only arylchlorocyclohexane **20** and arylcyclohexane **23** not incorporating the solvent were formed (paths *a*, *d*). In the presence of carbonate the enhanced nucleophilicity of the solvent led to ethers **24** and **25**, characterized by the rearrangement of the chain (paths *b*, *c*).

# Conclusion

Summing up, the efficiency of the photofragmentation of 4-chlorophenol and 4-chloroanisole shows a U-shaped dependence on the solvent polarity. Homolysis predominates in cyclohexane, heterolysis in alcohols. In ethyl acetate and acetonitrile the reaction is less efficient, apparently because the lifetime of the triplet state is shortened and makes homolysis less efficient, while heterolysis becomes significant only with the assistance by alcohols. This is consistent with sparse reports in previous literature.

The target of the investigation, however, was to determine whether photocleavage could be made useful for the arylation of alkenes and aromatics. This is indeed the case, and the products obtained are essentially the same from the phenol and from the anisole, thus discounting the hypothesis that 4-oxocylohexadienylidene (Scheme 1) has a role in this addition.<sup>21</sup> More precisely, two paths can be followed. In aprotic solvents an exciplex is formed and leads to arylation via an intimate radical ion pair. The adduct cation undergoes either deprotonation, giving allylbenzenes, or addition of the original nucleofuge, giving  $\beta$ -chloroalkylbenzenes. The proportion of the exciplex path is proportional to the nucleophilicity of the trap.

In contrast, alcohols as the solvent make unimolecular fragmentation of the triplet feasible<sup>22</sup> and give the

<sup>(18)</sup> For example, the quantum yield of photodegradation in MeOH is reported to be  $\Phi = 0.1$ , whereas in cyclohexane it is somewhat higher at  $\Phi = 0.35$ . See ref 11.

<sup>(19)</sup> Singlet aryl cation are to our knowledge obtained only from the photolysis of diazonium salt (see Gasper, S.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 5206–5211 and ref 4)

<sup>(20)</sup> Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini A. *Chem. Eur. J.* **2003**, *9*, 1549–1555.

<sup>(21)</sup> At any rate, the carbene would be expected to give isolable spirocyclopropylcyclohexadienones rather than alkylated phenols; see: Ershov, V. V.; Nikiforov, G. A.; de Jonge, C. R. *Quinone Diazides*; Elsevier: Amsterdam, 1981. Field, K. W.; Schuster, G. B. *J. Org. Chem.* **1988**, *53*, 4000–4006. Ohno, T.; Martin, N.; Knight, B.; Wudl, F.; Suzuki, T.; Yu, H. *J. Org. Chem.* **1996**, *61*, 1306–1309. Sander, W.; Kötting, C.; Hübert, R. *J. Phys. Org. Chem.* **2000**, *13*, 561–568. Becker, H. D.; Elebring, T. *J. Org. Chem.* **1985**, *50*, 1319–1322.

<sup>(22)</sup> The role of the formation of the hydrogen-halide bond in facilitating the heterolysis of the triplet has been demonstrated for 4-fluoroanilines. See: Freccero, M.; Fagnoni, M.; Albini, A. J. Am. Chem. Soc. **2003**, *125*, 13182–13190.

solvated phenyl cation. This is trapped by different  $\pi$ -nucleophiles with the same efficiency and gives the likewise solvated phenonium ion. As one may expect, the latter intermediate reacts with the solvent rather than with chloride and lives long enough to undergo typical hydride and alkyl rearrangements, particularly in ion stabilizing TFE.<sup>23</sup> In this poorly nucleophilic solvent the last step of the reaction is affected by the presence of a base, which increases formation of rearranged ethers.<sup>24</sup> However, cesium carbonate in some cases increases reduction in neat solvents.

It can be concluded that the photochemical arylation of alkenes and aromatics starting from chloroaromatics is not limited to chloroanilines and has been extended to 4-chlorophenol and 4-chloroanisole. The detailed course of the reaction and the products formed depend on conditions. In alcohols 4-hydroxy and 4-methoxyphenyl cations are involved, whereas in other solvents an exciplex/ion pair path is more appropriate. However, in both ways this novel arylation reaction appears to have synthetic significance as a mild, metal-free alternative to current methods<sup>26</sup> that may be carried out directly on phenols, skipping protection of the OH group.<sup>29</sup>

### **Experimental Section**

NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of <sup>1</sup>H and <sup>13</sup>C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. Cyclohexene, 2,3-dimethyl-2-butene, benzene, and compounds **1** and **2** were freshly distilled before use. The solvent was used as received. No previous anhydrification was carried out, since this did not affect the results.

The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes and a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission 310 nm) for the irradiation. The reaction course was followed by TLC (cyclohexanes-ethyl acetate) and GC by comparison with authentic samples. Workup of the photolytes involved concentration in vacuo and chromatographic separation.

**Irradiation of 1 and 2 in Neat Solvent. General Procedure.** A 0.05 M solution of **1** or **2** was irradiated in the

(25) Boule, P.; Guyon, C.; Lemaire, J. Chemosphere 1982, 11, 1179-1188.

(26) The formation of  $\beta$ -alkoxyalkylarenes is in common with the NOCAS reaction (see ref 27), but the scope is complementary (the NOCAS reaction applies to arylnitriles and not to electron-donating substituted aromatics) and the mechanism is opposite. Likewise, the  $S_{\rm RN}1$  reaction<sup>28</sup> applies to electrophilic but not nucleophilic alkenes.

(27) Mangion, D.; Arnold, D. R. Acc. Chem. Res. 2002, 35, 291–304.
 (28) Rossi, R. A.; Pierini, A. B.; Santiago, A. N. Org. React. 1999, 54, 1–271.

(29) Jackson, R. F. W.; Rilatt, I.; Murray, P. J. Org. Biomol. Chem. **2004**, *2*, 110–113.

solvent chosen (cyclohexane, ethyl acetate, MeCN, MeOH, or TFE) for 14 h; the same experiments were repeated in the presence of 0.025 M  $Cs_2CO_3$ , and product distribution was analyzed by GC. Phenol and anisole were determined on the basis of calibration curves. Preparative experiments were carried out only with TFE as the solvent (see below).

Irradiation of 1 in TFE. A solution of 95 mg of 1 (0.75 mmol) and 122 mg of  $Cs_2CO_3$  (0.0375 mmol) in 15 mL of TFE was irradiated for 26 h. Purification by column chromatography (cyclohexane/ethyl acetate 8:2) gave 43 mg of 3 (66% yield) and 9 mg of 2,4'-hydroxy-4-chlorobiphenyl  $4^{30}$  (6% yield, viscous oil, lit.<sup>6</sup> mp 118–119 °C). Data for 4: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.30 (m, 1H), 7.25 (m, 3H), 6.95 (m, 3H), 5.1 (bs, 1H), 5.0 (bs, 1H); IR (neat)  $\nu/cm^{-1}$  3360 (OH), 2950, 1688, 1591, 1507, 1231, 1496, 808. Anal. Calcd for  $C_{12}H_9ClO_2$ : C 65.32, H 4.11. Found: C 65.24, H 4.16.

Irradiation of 2 in TFE. A solution of 105 mg of 2 (0.75 mmol) and 122 mg of Cs<sub>2</sub>CO<sub>3</sub> (0.0375 mmol) in 15 mL of TFE was irradiated for 24 h (90% consumption of 2). Purification by column chromatography (cyclohexane/ethyl acetate 99:1) gave 29 mg of 5 (32% yield) and a mixture containing 37 mg of 2,4'-dimethoxy-4-chlorobiphenyl 631 (18% yield) and 20 mg of 4-(2,2,2-trifluoroethoxy)anisole  $\mathbf{8}^{32}$  (12% yield). A small amount of pure compound 8 was isolated by further chromatography separation. Data for 6: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture) & 7.5 (m, 1H), 7.45 (m, 1H), 7.25 (m, 1H), 6.65 (m, 1H), 6.90 (d, 2H, J = 8.5 Hz), 6.85 (m, 1H), 3.90 (s, 6H); IR (neat, from the mixture)  $\nu$ /cm<sup>-1</sup> 2935.6, 2338, 1713, 1610, 1246, 1225, 1029, 972, 831; MS (m/z) 248 (M<sup>+</sup>, 90), 198 (100). Data for 8: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.80–6.90 (m, 4H), 4.30 (q, 2H, J= 8 Hz), 3.80 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.0, 151.5, 124.0 (q, J = 275 Hz, CF<sub>3</sub>), 116.2 (CH), 114.7 (CH), 67.0 (q, J = 35 Hz), 55.6 (CH<sub>3</sub>); IR (neat) v/cm<sup>-1</sup> 2954, 1509, 1228, 1164, 826, 754. Anal. Calcd for C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>O<sub>2</sub>: C 52.43, H 4.40. Found: C 52.40, H 4.33. MS (m/z) 206 (M<sup>+</sup>, 60), 123 (100), 95 (50).

Irradiation of 1 and 2 in the Presence of  $\pi$  Nucleophiles. General Procedure. Experiments were carried out as described above starting from 190 mg of 1 or 210 mg of 2 (1.5 mmol, 0.05 M) in 30 mL of the chosen solvent after adding the  $\pi$  nucleophile (0.5 M of 2,3-dimethyl-2-butene and cyclohexene or 1 M of benzene). Two sets of experiments were carried out, the first one by irradiating for the same time as in neat solvent (14 h) and the latter by irradiating up to total consumption of the starting halide for the preparative experiments (see below). Reactions in the presence of equimolecular Cs<sub>2</sub>CO<sub>3</sub> were also tested, and the results are reported for the cases where an increase of the overall yield or a different photoproducts distribution were observed.

**Photochemical Reactions of 1 in the Presence of 2,3-Dimethyl-2-butene. In Cyclohexane.** After 14 h of irradiation (54% of consumption), purification (cyclohexane/ethyl acetate 8:2 as the eluant) of the raw photolisate afforded 18.3 mg of **3** (24% yield) and 25.6 mg of 2,3-dimethyl-3-(4-hydroxyphenyl)-1-butene (**9**, 18% yield, see below).

**In Ethyl Acetate.** After 23 h of irradiation, purification (cyclohexane/ethyl acetate 8:2 as the eluant) of the raw photolisate afforded 27.7 mg of **3** (20% yield) and 182 mg of **9** (colorless solid, mp 70–71 °C, 69% yield). Data for **9**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.75–7.20 (AA'BB', 4H), 4.85–5.00 (bs, 2H), 1.55 (s, 3H), 1.40 (s, 6H); IR (neat)  $\nu/\text{cm}^{-1}$  3286 (OH), 2960, 2378, 1551, 1432, 1370, 1230, 1176, 894, 830. Anal. Calcd for C<sub>14</sub>H<sub>19</sub>F<sub>3</sub>O<sub>2</sub>: C 60.86, H 6.93. Found: C 60.89, H 7.01.

**In Acetonitrile.** After 24 h of irradiation, purification (cyclohexane/ethyl acetate 8:2 as the eluant) of the raw photolisate afforded 12.6 mg of **3** (9% yield) and 177 mg of **9** (67% yield).

<sup>(23)</sup> The growing interest in the use of fluorinated alcohols in organic synthesis, as a result of the clean and selective reactions obtained, is apparent in a recent review: Bégué, J.-P.; Bonnet-Delpon, D.; Crousse, B. Synlett **2004**, 18–29.

<sup>(24)</sup> The effect of addition of cesium carbonate is complex. It somewhat enhances the conversion of chlorophenol 1, reasonably because some phenolate anion is then present, which absorbs a large proportion of the light used for irradiation (lamps centered at 310 nm) since its absorption is red-shifted by ca. 10 nm. This effect seems more important for 1 in polar nonprotic solvents despite the slight solubiblity of the base in this medium. In particular, in ethyl acetate the addition of cesium carbonate increased the conversion of 1 from 11% to 50%, with a concomitant increase of the photoreduction yield. Even if the phenolate absorbs part of the light, the photoproducts distribution did not change, in accord with previous reports.<sup>8a,25</sup> In accord with this rationalization, the reactivity of a nonacidic compound such as anisole 2 was affected to a much lower degree.

<sup>(30)</sup> Sarakha, M.; Bolte, M.; Burrows, H. D. *J. Phys. Chem. A* **2000**, *104*, 3142–3149.

<sup>(31)</sup> Nakamura, M.; Sawasaki, K.; Okamoto, Y.; Takamuku, S. J. Chem. Soc., Perkin Trans. 1 1994, 141–146.

<sup>(32)</sup> Camps, F.; Coll, J.; Messeger, A.; Pericas, M. A. *Synthesis* **1980**, 727–728.

**In Methanol.** After 14 h of irradiation, purification (cyclohexane/ethyl acetate 9:1 as the eluant) of the raw photolisate afforded 86 mg of **3** (61% yield) and 58 mg of **9** (22% yield).

The same reaction carried out in the presence of Cs<sub>2</sub>CO<sub>3</sub> (244 mg, 0.075 mmol, 0.025 M) afforded 63.4 mg of **3** (45% yield) and 80 mg of 2,3-dimethyl-2-(4-hydroxyphenyl)-3-methoxybutane (**10**, oil, 26% yield). Data for **10**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.75–7.35 (AA'BB', 4H), 3.15 (s, 3H), 1.35 (s, 6H), 1.03 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  153.1, 139.7, 129.6 (CH), 113.6 (CH), 78.5, 49.5 (CH<sub>3</sub>), 44.7, 24.4 (CH<sub>3</sub>), 19.8 (CH<sub>3</sub>); IR (neat)  $\nu/\text{cm}^{-1}$  3365 (OH), 2981, 2365, 1611, 1512, 1371, 1264, 1152, 1064, 832, 739. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>: C 74.96, H 9.68. Found: C 75.01, H 9.77.

In TFE. After 14 h of irradiation of the solution buffered with Cs<sub>2</sub>CO<sub>3</sub>, purification (cyclohexane/ethyl acetate 9:1 as the eluant) of the raw photolisate yielded 27 mg of **3** (19% yield), 114 mg of 2,3-dimethyl-3-(4-hydroxyphenyl)-1-butene (**9**, oil, 43% yield), and 51 mg of 2,3-dimethyl-3-(4-hydroxyphenyl)-3-(2,2,2-trifluoroethoxy)butane (**11**, oil, 12% yield). Data for **11**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.75–7.35 (AA'BB', 4H), 3.65 (q, 2H, J = 8 Hz), 1.40 (s, 6H), 1.05 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  153.3, 129.5 (CH), 127.2 (q, J = 275 Hz, CF<sub>3</sub>), 113.7 (CH), 109.15, 80.4, 60.5 (q, J = 35 Hz), 44.6, 24.2 (CH<sub>3</sub>), 20.4 (CH<sub>3</sub>); IR (neat)  $\nu/\text{cm}^{-1}$  3355 (OH), 2975, 1612, 1514, 1377, 1280, 1162, 972, 831. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O: C 81.77, H 9.15. Found: C 81.71, H 9.17.

Photochemical Reactions of 2 in the Presence of 2,3-Dimethyl-2-butene. In Cyclohexane. After 26 h of irradiation, purification (eluant changing form neat cyclohexane to cyclohexane/ethyl acetate 98:2 mixtures) of the raw photolisate afforded 2.3 mg of 5 (2% yield) and a mixture containing 95.3 mg of 2,3-dimethyl-3-(4-methoxyphenyl)-1-butene 12<sup>33</sup> (34% yield, see below) and 10 mg of 2,3-dimethyl-2-(4-methoxyphenyl)butane (13, 4% yield). Data for 13: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.80–7.30 (AA'BB', 4H), 3.80 (s, 3H), 1.25 (s, 6H), 0.75 (d, 6H, J = 9 Hz); MS (m/z) 192 (M<sup>+</sup>, 2), 149 (100), 121 (28); IR (neat, for the mixture)  $\nu/cm^{-1}$  2929, 1611, 1514, 1448, 1247, 1178, 1095, 1038, 820.

**In Ethyl Acetate.** After 23 h of irradiation, purification (eluant changing from neat cyclohexane to cyclohexane/ethyl acetate 98:2 mixtures) of the raw photolisate afforded 11.3 mg of **5** (7% yield) and 154 mg of **12** (54% yield). Data for **12**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.80–7.30 (AA'BB', 4H), 4.90 (bs, 1H), 5.00 (bs, 1H), 3.80 (s, 3H), 1.60 (s, 3H), 1.45 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  157.4, 152.8, 140.4, 127.0 (CH), 113.2 (CH), 109.2 (CH<sub>2</sub>), 55.1 (CH<sub>3</sub>), 43.1, 28.4 (CH<sub>3</sub>), 20.0 (CH<sub>3</sub>); IR (neat)  $\nu/\text{cm}^{-1}$  2968, 1610, 1512, 1250, 831; MS (m/z) 190 (M<sup>+</sup>, 49), 175 (91), 149 (100), 121 (44). Anal. Calcd for C<sub>13</sub>H<sub>18</sub>O: C 82.06, H 9.53. Found: C 81.99, H 9.51.

**In Acetonitrile.** After 26 h of irradiation, purification (cyclohexane/ethyl acetate 98:2 as the eluant) of the raw photolisate afforded 4 mg of 5 (2% yield) and 139 mg of 12 (49% yield).

In Methanol. After 16 h of irradiation of the solution buffered with Cs<sub>2</sub>CO<sub>3</sub>, purification (cyclohexane/ethyl acetate 99:1 as the eluant) of the raw photolisate yielded 35.7 mg of 5 (22% yield) and two fractions containing 45 mg of 12 (16% yield), 48 mg of 13 (17% yield) and 55 mg of 2,3-dimethyl-2-(4-methoxyphenyl)-3-methoxybutane (14, 17% yield). Further purification of the fractions containing product 14 afforded a pure sample of such compound. Data for 14: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.80–7.40 (AA'BB', 4H), 3.8 (s, 3H), 3.15 (s, 3H), 1.4 (s, 6H), 1.05 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  157.2, 139.5, 129.4 (CH), 112.9 (CH), 78.5, 55.0 (CH<sub>3</sub>), 49.4 (CH<sub>3</sub>), 32.4, 24.4 (CH<sub>3</sub>), 17.8 (CH<sub>3</sub>); IR (neat)  $\nu/cm^{-1}$  2973, 1611, 1513, 1250, 832. Anal. Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: C 75.63, H 9.97. Found: C 75.53, H 10.01.

In TFE. After 14 h of irradiation of the solution buffered with  $Cs_2CO_3$ , purification (cyclohexane/ethyl acetate 99:1 as the eluant) of the raw photolisate yielded 19.5 mg of **5** (12% yield) and two fractions: the first contained 60 mg of **12** (21% yield) and 41 mg of **13** (14% yield), and the second 74 mg of 2,3-dimethyl-3-(4-methoxyphenyl)-3-(2,2,2-trifluoroethoxy)bu-

tane (**15**, 17% yield) and 36 mg of 2-(4-methoxyphenyl)-2-(2,2,2-trifluoroethoxy)-3,4-dimethylbutane (**16**, 8% yield). Data for **15**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.80–7.30 (AA'BB', 4H), 3.8 (s, 3H), 3.65 (q, 2H, J = 8 Hz), 1.4 (s, 6H), 1.05 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  153.3, 138.9, 129.9, 124 (q, J = 270 Hz, CF<sub>3</sub>), 112.7 (CH), 80.5, 60.2 (q, J = 35 Hz), 55.2 (CH<sub>3</sub>), 44.6, 24.9 (CH<sub>3</sub>), 20.4 (CH<sub>3</sub>); MS (m/z) 191 (M-CF<sub>3</sub>CH<sub>2</sub>O, 19), 149 (16), 73 (100). Data for **16**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.85–7.40 (AA'BB', 4H), 3.85 (s, 3H), 3.65 (q, 2H, J = 8 Hz), 1.6 (s, 3H), 0.9 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  158.3, 132.9, 129.3 (CH), 124 (q, J = 270 Hz, CF<sub>3</sub>), 112.6 (CH), 84.3, 66.3 (q, J = 35 Hz), 55.2 (CH<sub>3</sub>), 38.7, 25.4 (CH<sub>3</sub>), 18.9 (CH<sub>3</sub>). IR, (neat, for the mixture)  $\nu/cm^{-1}$  2974, 1611, 1513, 1281, 1248, 1162.

**Photochemical Reactions of 1 in the Presence of Cyclohexene. In Cyclohexane.** After 14 h of irradiation (48% of consumption), phenol **3** (21% yield) and traces of compound **17** (see below) were detected by GC analysis. Further irradiation did not increase the amount of the arylated product.

In Ethyl Acetate. After 24 h of irradiation, purification (cyclohexane/ethyl acetate 9:1 as the eluant) of the raw photolisate afforded 38 mg of **3** (24% yield) and 70 mg of *trans* 1-(*p*-hydroxyphenyl)-2-chlorocyclohexane (**17**, 20% yield, colorless solid, mp 127–128 °C). Data for **17**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.9–7.1 (AA'BB', 4H), 3.9 (dt, 1H, J = 4 and 12 Hz), 2.6 (dt, 1H, J = 4 and 12 Hz), 2.6 (dt, 1H, J = 4 and 12 Hz), 2.6 (dt, 1H, J = 4 and 12 Hz), 2.6 (dt, 1H, J = 4 and 12 Hz), 2.6 (dt, 1H, J = 4 and 12 Hz), 2.6 (dt, 1H, J = 4 and 12 Hz), 2.6 (CL), 3  $\delta$  154.0, 136.2, 128.4 (CH), 115.1 (CH), 64.7 (CH), 52.6 (CH), 37.1 (CH), 2928, 1611, 1513, 1448, 1247, 1150, 826. Anal. Calcd for C<sub>12</sub>H<sub>15</sub>ClO: C 68.41, H 7.18. Found: C 68.50, H 7.08. The assignment of the *trans* configuration was based on the high value (12 Hz) of the coupling constant between H1 and H2 in the cyclohexane ring.

**In Acetonitrile.** After 24 h of irradiation, purification (cyclohexane/ethyl acetate 9:1 as the eluant) of the raw photolisate afforded 25 mg of **3** (18% yield) and 38 mg of **17** (12% yield).

In Methanol. A solution of 190 mg (1.5 mmol, 0.05 M) of 1, 1.6 mL (15 mmol, 0.5 M) of cyclohexene in 30 mL of MeOH was irradiated for 14 h. Solvent was removed ,and the resulting raw photolisate was dissolved in 10 mL of DMF and treated with 300 mg of CaCO<sub>3</sub> and 400  $\mu$ L (6 mmol) of CH<sub>3</sub>I. The resulting solution was stirred for 3 h, diluted with 20 mL of water, and extracted with Et<sub>2</sub>O. The crude product obtained was purified by column chromatography (cyclohexane/ethyl acetate 99:1) affording 67 mg of 5 (62% yield) and a mixture (resolved by NMR spectroscopy) containing 26 mg of 1-(1-(pmethoxyphenyl)-1-methoxy)methylcyclopentane (19, 8% yield) and 12 mg of trans 1-(p-methoxyphenyl)-2-chlorocyclohexane (20,<sup>34</sup> 4% yield, see below). Data for 19: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, from the mixture)  $\delta$  6.9–7.4 (AA'BB' 4H), 3.78 (d, 1H, J = 9Hz), 3.8 (s, 3H), 2.9 (s, 3H), 2.1 (m, 1H), 1.2-2.0 (m, 8H); <sup>13</sup>C NMR ((CD<sub>3</sub>COCD<sub>3</sub>) & 158.5, 137.9, 127.0 (CH), 113.2 (CH), 87.6 (CH), 55.4 (CH<sub>3</sub>), 46.9 (CH<sub>3</sub>), 46.9 (CH), 35.2 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 21.7 (CH<sub>2</sub>). IR, (neat, for the mixture) v/cm<sup>-1</sup> 2838, 1611, 1513, 1459, 1278, 1250, 1115, 1037, 970, 830.

In TFE. After 24 h of irradiation, purification (cyclohexane/ ethyl acetate 9:1 as the eluant) of the raw photolisate afforded 42 mg of **3** (30% yield) and mixtures containing 24 mg of **17** (8% yield), 24.5 mg of 1-(1-(*p*-hydroxyphenyl)-1-(2,2,2-trifluoroethoxy)methylcyclopentane (**21**, 6% yield), and 16.5 mg of 1-(*p*-hydroxyphenyl)-1-(2,2,2-trifluoroethoxy)cyclohexane (**22**, 4% yield). Data for **21**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, from the mixture)  $\delta$  6.8–7.4 (AA'BB', 4H), 4.1 (m, 1H), 3.7 (q, 2H, *J* = 9 Hz), 2.2 (m, 1H), 1.1–1.8 (m, 8H); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ 156.7, 135.1, 135.0 (q, CF<sub>3</sub>, *J* = 275 Hz), 127.3 (CH), 114.8 (CH), 87.4 (CH), 64.7 (q, CH<sub>2</sub>, *J* = 35 Hz), 46.5 (CH), 35.6

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(CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>). Data for **22**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, from the mixture)  $\delta$  6.8–7.1 (AA'BB', 4H), 3.6 (q, 2H, J = 9 Hz), 2.1 (m, 2H), 1.1–1.8 (m, 8H); <sup>13</sup>C NMR (CD<sub>3</sub>-COCD<sub>3</sub>)  $\delta$  157.2, 135.0 (q, CF<sub>3</sub> J = 275 Hz), 131.0, 128.1 (CH), 115.0 (CH), 59.9 (q, CH<sub>2</sub>, J = 35 Hz), 35.0 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 21.5 (CH<sub>2</sub>). IR (neat, for the mixture of **21** and **22**)  $\nu$ /cm<sup>-1</sup> 3356 (OH), 1638, 1612, 1513, 1438, 1364, 1236, 994, 915, 827.

The same reaction carried out in the presence of  $Cs_2CO_3$ and irradiated for 14 h afforded 61.5 mg of **3** (44% yield), a mixture containing 37.5 mg of **17** (12% yield), 54 mg of 1-(1-(*p*-hydroxyphenyl)-1-(2,2,2-trifluoroethoxy)methylcyclopentane (**21**, 13% yield).

**Photochemical Reactions of 2 in the Presence of Cyclohexene. In Cyclohexane.** After 26 h of irradiation, purification (cyclohexane as the eluant) of the raw photolisate gave 26 mg of 5 (16%) and 125.4 mg of **20** (38%, oil). Data for **20**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.8–7.2 (AA'BB', 4H), 4.2 (dt, 1H, J= 4 and 11 Hz), 3.8 (s, 3H), 2.7 (dt, 1H, J = 4 and 11 Hz), 2.3 (m, 1H), 2.1 (m, 1H), 1.8 (m, 3H), 1.6 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.3, 136.3, 128.5 (CH), 113.4 (CH), 64.5 (CH), 54.9 (CH<sub>3</sub>), 52.7 (CH), 37.9 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>); IR (neat) ν/cm<sup>-1</sup> 2932, 1610, 1511, 1459, 1247, 1178, 1074, 1039, 829. Anal. Calcd for C<sub>13</sub>H<sub>17</sub>ClO: C 69.48, H 7.62. Found: C 69.34, H 7.52. MS (*m*/*z*) 224 (M<sup>+</sup>, 50), 189 (10), 147 (100), 121 (45), 91 (32). The assignment of the *trans* configuration was based on the high value (11 Hz) of the coupling constant between H1 and H2 in the cyclohexane ring.

**In Ethyl Acetate.** After 23 h of irradiation, purification (cyclohexane as the eluant) of the raw photolisate gave 24 mg of **5** (15%) and 115 mg of **20** (32%).

**In Acetonitrile.** After 24 h of irradiation, purification (cyclohexane as the eluant) of the raw photolisate gave 41 mg of **5** (26%) and 73 mg of **20** (20%).

In Methanol. After 24 h of irradiation, purification (cyclohexane as the eluant) of the raw photolisate gave 26.5 mg of 5 (18% yield) and a mixture containing 104 mg of 18 (32% yield) and 48 mg of 19 (15% yield). Data for 18: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.90–7.20 (AA'BB', 4H), 3.80 (s, 3H), 3.15 (s, 3H), 2.10–2.20 (m, 2H), 1.20–1.80 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  159.0, 134.0, 128.2 (CH), 113.3 (CH), 76.3, 54.4 (CH<sub>3</sub>), 48.3 (CH<sub>3</sub>), 35.2 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 21.7 (CH<sub>2</sub>); IR (neat, for the mixture)  $\nu$ /cm<sup>-1</sup> 2932, 2856, 1609, 1512, 1463, 1248, 1178, 1038, 825, 737.

**In TFE.** After 26 h of irradiation (80% conversion), purification (cyclohexane as the eluant) of the raw photolisate afforded 14 mg of **5** (11% yield) and a mixture containing 80 mg of **20** (29% yield) and 105 mg of *p*-methoxyphenylcyclohexane (**23**,<sup>35</sup> 45%). Data for **23**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.80– 7.15 (AA'BB', 4H), 3.77 (s, 3H), 3.15 (s, 3H), 2.10–2.20 (m,

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2H), 1.20–1.80 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  157.5, 140.3, 127.5 (CH), 113.6 (CH), 55.1 (CH<sub>3</sub>), 48.3 (CH<sub>3</sub>), 35.2 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 21.7 (CH<sub>2</sub>); IR (neat, for the mixture)  $\nu/\text{cm}^{-1}$  2928, 2855, 2363, 1610, 1512, 1247, 1178, 1037, 824; MS (*m*/*z*) 190 (M<sup>+</sup>, 60), 147 (100), 134 (30), 121 (56), 91 (45), 43 (45).

The same reaction carried out in the presence of Cs<sub>2</sub>CO<sub>3</sub> and irradiated for 14 h yielded 26 mg of 5 (10% yield), 25 mg of **20** (9% yield) and a mixture containing 84 mg of 1-(pmethoxyphenyl)-1-(2,2,2-trifluoroethoxy)cyclohexane (24, 20% yield) and 89.4 mg of 1-(1-(p-methoxyphenyl)-1-(2,2,2-trifluoroethoxy)methylcyclopentane (25, 21% yield). Data for 24: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.8–7.2 (AA'BB', 4H), 3.8 (s, 3H), 3.6 (m, 2H), 2.15 (m, 2H), 1.1-1.8 (m, 8H); <sup>13</sup>C NMR  $(CDCl_3) \delta 159.8, 135.8, 135.0 (q, CF_3, J = 275 Hz), 128.1 (CH),$ 113.7 (CH), 60.9 (q, CF<sub>3</sub>, J = 35 Hz), 29.2 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 22.1 (CH<sub>2</sub>). Data for25: <sup>1</sup>H NMR (CDCl<sub>3</sub>, from the mixture)  $\delta$  6.8–7.3 (AA'BB', 4H), 4.1 (d, 1H, J = 9 Hz), 3.8 (s, 3H), 3.6 (m, 2H), 2.1 (m, 1H), 1.1-1.8 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  158.8, 136.3, 135.0 (q, CF<sub>3</sub>, J = 275Hz), 128.1 (CH), 113.6 (CH), 87.8 (CH), 65.6 (q, CH<sub>2</sub>, J = 35 Hz), 46.7 (CH), 29.8 (CH<sub>2</sub>), 27.3 (CH<sub>2</sub>), 22.1 (CH<sub>2</sub>), 21.3 (CH<sub>2</sub>). IR (neat, for the mixture)  $\nu/cm^{-1}$  2969, 1638, 1612, 1512, 1438, 1364, 1236, 994, 915, 827.

Photochemical Reactions of 1 in the Presence of Benzene. In TFE. A solution of 190 mg (1.5 mmol, 0.05 M) of 1, 2.7 mL (30 mmol, 1 M) of benzene in 30 mL of TFE was irradiated for 24 h. Purification by column chromatography (cyclohexane/ethyl acetate 8:2) afforded 23 mg of 3 (16% yield) and 168 mg of 4-phenylphenol (26,  $^{36}$  66% yield) as a colorless solid, mp 163–165 °C (lit. 165 °C Acros-organics), with spectroscopic characteristics identical to those of an authentic sample.

**Photochemical Reactions of 2 in the Presence of Benzene. In TFE.** A solution of 210 mg (1.5 mmol, 0.05 M) of **2**, 2.7 mL (30 mmol, 1 M) of benzene in 30 mL of TFE was irradiated for 24 h (90% consumption). Purification by column chromatography (cyclohexane/ethyl acetate 9:1) afforded 10 mg of **5** (6%) and 193 mg of 4-phenylanisole (**27**, 70%). Crystallization from hexane gave a colorless solid, mp 81–83 °C (lit.<sup>37</sup> 90–90.5 °C). Spectroscopic data were in accordance with the literature.<sup>38</sup>

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